

Adhesion Measurement of Films and Coatings

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ADHESION MEASUREMENT OF FILMS AND COATINGS

Editor: K.L. Mittal

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Preface

This book embodies the proceedings of the International Symposium on Adhesion Measurement of Films and Coatings held in Boston, 5–7 December, 1992 under the auspices of Skill Dynamics, an IBM Company. Apropos, the papers from this symposium were earlier published in three issues of the *Journal of Adhesion Science and Technology* as follows: Vol. 7, No. 8 (1993); Vol. 7, No. 12 (1993); and Vol. 8, No. 6 (1994) except the opening article by yours truly. As researchers and technologists evinced considerable interest in acquiring these special issues separately, so we decided to make available a hard-bound book chronicling in one place the acta of this symposium. It should be recorded for historical reasons that the premier symposium on this topic was held in 1976 under the aegis of the American Society for Testing and Materials (ASTM).

Films and coatings are used for a variety of purposes and their adequate adhesion to the underlying substrates, *inter alia*, is of cardinal importance from practical consideration. Concomitantly, the need for techniques for quantitative measurement of adhesion becomes quite patent.

Since the first symposium was held in 1976, there has been brisk activity in devising new ways to measure adhesion or ameliorating the existing repertoire. A legion of techniques, ranging from very mundane to very sophisticated, have been documented in the literature for adhesion measurement of films and coatings. Recently I had the occasion to sift the literature and compile the list of adhesion measurement techniques and, you may believe or not, the final score came to 355 (quite a stupendous number), which are listed in the opening paper in this book. However, it should be mentioned that certain techniques might be listed more than once because of different appellations given to these. It is interesting to note that some of these techniques sound uncouth, primitive and plainly humorous. In spite of this cornucopia of techniques, no single technique has been acceptable to everyone or applicable to all coating-substrate combinations; and this has been the cause for the proliferation of techniques for adhesion measurement. Also there has been a perennial discordance among the people working in this arena as to what exactly is measured when someone uses one of these techniques to measure adhesion.

So in light of the long hiatus since the first symposium coupled with the fact that there was a high tempo of activity and tremendous interest in this topic, the need for another symposium became abundantly evident. Also, most of the people I polled felt that such a symposium was long overdue.

This symposium was planned with the following objectives in mind (i) to bring together the community interested in this topic, (ii) to provide a forum for discussion of latest developments, (iii) to provide an opportunity for cross-pollination of ideas; and (iv) to identify the vexing problems, as well as the techniques which offered good promise and warranted vigorous pursuit. When the announcement of this symposium was sent out, it elicited an excellent response and concomitantly the technical program comprised 51 presentations (overviews as well as original research results). A number of techniques were discussed, a great deal of information was covered, and there were illuminating (not exothermic) discussions throughout the course of this symposium. If comments from the attendees is a barometer of the success of the event, then this symposium was a huge success.

I certainly hope this book will provide bountiful current information on techniques for adhesion measurement of films and coatings, and will be found useful by both veterans and neophytes interested in this subject.

K. L. Mittal

Adhesion measurement of films and coatings: a commentary

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Abstract—The adhesion of thin films and coatings is of paramount importance in many and diverse technologies; concomitantly, the need to measure adhesion is quite patent. Recently there has been a flurry of activity in devising new or ameliorating the existing techniques for adhesion measurement of films and coatings. As a matter of fact, a cornucopia of methods is available, ranging from very mundane or primitive to very sophisticated. Some techniques have been claimed to measure ‘interfacial adhesion.’ However, in most situations, strictly speaking, there exists no interface to start with, so what is the significance of interfacial adhesion? Actually what is measured is the so-called practical adhesion, defined as the force or the work required to remove a film or coating from the substrate, irrespective of the locus of failure. Alternatively, practical adhesion can be expressed as the time required for removal or delamination of a film or coating under accelerated stress conditions (e.g. exposure to boiling water, solvents, corrosives, etc.). In a film or coating-substrate combination, the failure will take place at the weakest place and could be interfacial (rare), interphasial, or cohesive. Here the concept and significance of practical adhesion, and its relationship to the fundamental or intrinsic adhesion is discussed. Some comments are made on the locus of failure. A comprehensive list of documented techniques for adhesion measurement of films and coatings is provided.

1. INTRODUCTION

Films and coatings are used in a legion of technologies for a variety of purposes, and irrespective of their intended function these must adhere satisfactorily to the underlying substrate. So the need for quantitative assessment of thin film or coating adhesion is quite patent. Many techniques for adhesion measurement of thin films and coatings [1, 2] have been documented, and even a cursory look at the recent literature will show that there is a tremendous activity in this domain. This proceedings volume is a good testimonial to the brisk activity in the arena of adhesion measurement. Apropos, the difference between a film and coating is: A film is a thin coating and a coating is a thick film; it really is a matter of thickness. There is no universal agreement or standard on the upper limit of thickness of a thin film, but generally speaking thin films are of the order of 100 nm or even less. Many of the adhesion measurement techniques apply to both films and coatings, but some may be more specific to one or the other. In this paper, the terms film and coating will be used interchangeably.

2. WHAT IS ACTUALLY MEASURED?

This question is extremely important as there has been and there still is a great deal of confusion about what exactly is measured when one attempts to measure adhesion of a film or coating. The answer depends on the definition of adhesion.

Adhesion can be manifested in three different forms [3]: (i) Fundamental Adhesion, (ii) Thermodynamic Adhesion, and (iii) Practical Adhesion. Fundamental Adhesion is defined as the summation of all interfacial intermolecular interactions between the contacting materials. If one knows the type of interaction between the film material and the substrate and the number of interacting units per unit area, then one can calculate the fundamental adhesion. Conversely, fundamental adhesion represents the energy required to break chemical bonds at the weakest plane in the film-substrate adhering system under the adhesion measurement conditions used. However, it should be noted that these two forms of fundamental adhesion could be quite different as the former refers to contact formation and the latter represents contact break, and the weakest plane during the disruption of an adhering system may not be where the contact was initially formed. In the following discussion it is the latter form of fundamental adhesion which is relevant. Thermodynamic adhesion signifies the change in free energy when an interface is formed (or separated) and is expressed as $W_A = \gamma_{S1} + \gamma_{S2} - \gamma_{S1S2}$, where W_A is the work of adhesion and γ_{S1} and γ_{S2} represent the surface free energies of material 1 (substrate) and material 2 (film), respectively. γ_{S1S2} is the interfacial free energy. In case of liquid coatings, W_A can be easily determined by $W_A = \gamma_{LV}(1 + \cos\theta)$, where γ_{LV} is the surface free energy of the liquid, and θ is the contact angle of the liquid coating on the substrate.

The practical adhesion signifies the force or the work required to remove or detach a film or coating from the substrate irrespective of the locus of failure (see further discussion regarding this issue in Section 3). Actually this is what is measured when one attempts to measure adhesion by any of the more than 300 techniques. This includes the energy required to deform both the film or coating and the substrate, as well as the energy dissipated as heat or stored in the film or coating, and the component representative of the actual fundamental adhesion. The relationship between the practical adhesion and the fundamental adhesion is expressed as follows:

$$\text{Practical adhesion} = f (\text{fundamental adhesion, other factors}).$$

A myriad of 'other factors' influence the practical adhesion of a coating or film. Some of these are: stress in the film or coating; thickness and mechanical properties of the coating; mechanical properties of substrate; work consumed by plastic deformation and viscous dissipation; mode of failure; mode and rate of applying the force or the energy to detach the film, i.e. the technique used for adhesion measurement, and the parameters of the technique. Let me cite the example of peel test, which is one of the commonly used techniques. For the same film-substrate combination, different angles and rates of peel culminate in different peel strength values; although the fundamental adhesion is expected to be the same irrespective of the angle or rate of peel. This behavior can be easily explained by the above expression in that the first

quantity (fundamental adhesion) is the same but the contribution due to 'other factors' is quite different at different angles and different rates. At higher rates of peel, for example for viscoelastic materials, the peel strength is generally higher because of more viscoelastic dissipation of energy.

Also even for the same film–substrate combination, different measurement techniques yield different results. Hull *et al.* [4] published very interesting results in this regard. They studied the effect of thickness of gold film (up to 500 nm) on silicon substrate by peel, pull and scratch tests. They found that peel force decreased with thickness; whereas both pull strength and scratch force increased with thickness but in different manners: linear in the case of scratch test and non-linear when pull test was employed. This clearly shows that different techniques involve different parameters; and, concomitantly, culminate in different practical adhesion values. However, all this can be explained by the expression delineated above.

In a multilayer system, the failure will take place at the weakest plane. Concomitantly, the practical adhesion is the net result of the energy required to break chemical bonds at the weakest place and the contribution due to other factors.

In the discussion above, there has been an implicit assumption that there is an interface to start with and a clear-cut interfacial separation takes place. Strictly speaking, an interface is a mathematical plane or a sharp frontier with no thickness, and the existence of such an interface and a veritable interfacial separation is a rare occurrence. In a situation where one could observe a true interfacial separation, then in that case the fundamental adhesion could be labeled as 'fundamental interfacial adhesion'. However, in most situations, an interphasial separation is the norm (see the next section for further discussion on this topic). So in the case of separation in the interphase or interfacial region, the fundamental adhesion denotes the energy required to break chemical bonds at the weakest place in the interphase. Apropos, some people refer to 'fundamental adhesion' as 'intrinsic adhesion' and the contribution due to other factors as 'extrinsic adhesion.' Intrinsic or fundamental adhesion represents the chemical component as it is dictated by the prevailing chemistry at the weakest place, and the contribution due to other factors constitutes 'non-chemical' or 'mechanical' component.

So it is quite manifest from this discussion that all these techniques measure the cumulative effect of intrinsic or fundamental adhesion and the contribution due to many other factors. One may ask the question: Can one determine fundamental adhesion by making practical adhesion measurement? I do not think so, as it is very difficult, maybe impossible, to quantitate the contribution due to the multitude of non-chemical factors. One can only hope to see increase in practical adhesion by improving fundamental adhesion (by manipulating the interphase, or interface, if it exists) provided no adverse conditions are present (e.g. stresses in the film). However, it would be nice to have a nondestructive and quantitative way to determine fundamental or intrinsic adhesion.

To conclude this section, some comment should be made regarding failure in the bulk of the coating, i.e. cohesive failure. Strictly speaking if the coating fails in the bulk that is really a problem of strength of materials and transcends the purview of

adhesion science. As a corollary, in the case of bulk coating failure, attempts to improve the interface or interphase will be futile.

3. LOCUS OF FAILURE

When a film is detached from a substrate, the important question is: Where does the failure take place? It could be at the interface, in the interphase, or in the bulk (called cohesive failure) of the film or the substrate. As mentioned above a true interfacial failure is very uncommon as most often there is no clear-cut interface to start with. Most often failure occurs in an interphase or an interfacial region which has some thickness. Incidentally an interphase could be a single layer or region, or a combination of many regions with differing properties. The interphases are real and they may be present naturally (e.g. oxide on a metal) or are created deliberately (use of intermediate layers or adhesion promoters, surface treatment layers) or are formed by interaction or interdiffusion of the film material with the substrate or by migration of a new component (e.g. plasticizer) from the bulk of one of the adhering materials. It should be kept in mind that interphases have characteristics different from both bulk substrate and bulk coating.

Now the logical question is: If the failure occurs in the interphase, should it be called failure related to adhesion, or is it a bulk failure? This is a moot point and there is actually no easy answer to it. However, most adhesionists will agree that an interphasial failure falls within the purview of practical adhesion. In other words, practical adhesion signifies the force or the work required to detach a film from the substrate if the locus of failure is interfacial, or interphasial. Of course, if there is clear-cut failure in the bulk of the film (i.e. a uniform layer of bulk film material is left behind on the substrate after detachment of the film) that is a patent case of cohesive failure. However, quite often people just measure the force or the energy required to detach a coating without precisely determining the locus of failure, and even a bulk (cohesive) failure can be misconstrued (depending on the technique used to investigate the locus of failure) as interfacial, or interphasial failure. From a pragmatic point of view, the main interest is what sort of force or work a given film–substrate combination can withstand before delamination, irrespective of where it fails. With that in mind, it makes sense to define practical adhesion as the force or the work required to detach a coating or film from the substrate irrespective of the locus of failure. However, to improve practical adhesion, it is imperative to know precisely the locus of failure, so suitable approach can be taken to strengthen the weakest link.

Incidentally, it should be kept in mind that conclusion as to the precise locus of failure depends on the analytical technique used to examine the failed components of an adhering system. If an unaided eye is used to see if there is any film material left on the substrate then one may conclude that there was clearly an interfacial separation even if a thin layer of film was still clinging to the substrate because the human eye cannot see it. On the other hand, examination by sensitive surface spectroscopic analysis techniques will ‘see’ this thin layer and concomitantly one

will conclude that the film failed, which signifies cohesive failure. Or if some other technique (e.g. microscopic) were used one may come to a different conclusion. So it is imperative that one must specify how the failed components were examined when one comments on the locus of failure.

4. ADHESION MEASUREMENT TECHNIQUES

As pointed out in the Introduction, a legion of techniques have been documented in the literature for adhesion measurement of films and coatings. Table 1 provides an alphabetical listing of such techniques. A few comments about this long list of techniques are in order. (i) They range from inexpensive to very sumptuous, and from very primitive to very sophisticated. (ii) Some of these methods are qualitative in nature, so no numerical values can be obtained. (iii) Most of these are mechanical and destructive in nature, and (iv) Just the sheer size of the table shows tremendous interest and activity in the topic of adhesion measurement. It should be noted that certain techniques might be listed more than once because of the different appellations given to these.

Table 1.

Techniques for adhesion measurement/assessment/monitoring of films and coatings

Ablation
Abrasion
Acceleration
Acceleration–Deceleration
Acoustic Emission
Acoustic Microscopy
Adherometer
Adherometer–Integrometer
Adhesive Tape
Angular Scribe-Stripping
Applied Moment
ARCO Microknife
ASTM Tensile Adhesion Method
Automatic Scrape
Balanced-Beam Scrape
Bathroom
Bell Tester
Bend
Bend (180°)
Bend (180°) + Tape
Bending (Three-point, or Four-point)
Bend-Peel Test
Bend Test (ASTM 571-72)
Black Lead Pencil
Blade
Blade Cutting Adhesion Tester

Table 1.

(Continued)

Blister (Constrained, Island)
Blister Peel
Boiling Water
Bolt Tensile
Both Sides Pull
Brenner Nodule Test
Brown and Garnish Crosshatch-Metal Strip Tape Test
Bubble
Buckling
Buffing
Bullet
Burgess Method
Burnishing
Can opener
Capacitance Measurement
Capacity Test
Cathodic Treatment
Centrifugal Hammer
Chisel
Chisel-Knife
Cleavage
Coin Scratch
Compact Tension
Compression
Conical Head Tensile
Conical Mandrel
Conical Mandrel + Tape
Constant Strain (<i>in-situ</i> SEM)
Constrained Blister
Continuous Indentation
Creep
Crosscut
Cross-cut Tape Test (ASTM D 3359-78)
Crosshatch
Crosshatch, Impact + Tape
Crosshatch + Tape
Crosshatch Without Tape
Crowfoot Knife Test
Cunningham Wood Cross Adhesion Test
Cupping
Cupping and Indentation
Cutting
Damping (resonator)
Deep Draw
Deformation
Delamination
Diamond Indentation Draw (DID)
Diamond Scratch

Table 1.

(Continued)

Die Bond Pull
Dielectrometric
Direct Pull
Disc-On-Disc (DOD)
Dishwasher
Distensibility
Dome
Dot
Double Cantilever Adhesion Test
Double Cantilever Beam
Double Torsion
Draw
Driven Blade Tester
DuPont Sharp Tool
Dynamic
Dynamic Response (based on)

Edge Delamination
Elcometer Adhesion Tester
Electrochemical
Electromagnetic Tensile
Electron Beam (Pulsed)
Electron Spin Resonance
Elongation
Erosion
Exposure + Tape

File
Fingernail
Flat-Wise Tension Test
Flexure
Flexure Spallation Test
Flexure Strain
Floating Image
Fluorescent
Flyer Plate
Ford Motor Co. Crosshatch Tape Test
Four-Point Bend
Fracture Energy
Fracture Mechanics Test
Freeze-Thaw Cycle
Friction (Internal)

Gardner-van Heuckeroth Adhesion Test
General Electric Plug Method
Graham-Linton Edge Test
Gravelometer
Grind-Saw
Grindwheel
Groove

Table 1.
(Continued)

Hammering
 Hardness
 Heating and Quenching
 Hesiometer
 Hoffman Scratch Tester
 Hot Water
 Hounsfield Tensiometer
 Hydraulic Adhesiometer
 Hydrodynamic
 Hydrophil Balance

 I-Beam
 Ice Pick
 ICI Bullet
 ICI Gun
 $\bar{I} \times \bar{H}$
 Impact
 Impact Deceleration
 Impact + Tape
 Impulse
 Inboard Wire Peel
 Indentation
 Indentation-Debonding
 Inertia
 Inflated membrane
In-situ SEM Constant Strain Method
 Interchemical Adherometer
 Internal Friction
 Internal Stress of Ni film
 Interrupted Bend Test
 Inverse Ollard Method
 Inverse peel
 Inverted Blister
 Ion-Migration
 Island Blister

 Jacquet Method

 Knife
 Konig Knife-Wedge
 Koole Chisel

 Lamb Waves (use of)
 Lap Shear
 Laser Ablation
 Laser Acoustic Test
 Laser Beam Holography
 Laser Spallation
 Liquid Jet
 Liquid Wedge
 LSRH-Revetest

Table 1.

(Continued)

Mandrel
Mechanical Resonance Method
MEEM
Membrane (Inflated)
Meredith and Guminski Chisel
Meredith-Guminski Adhesion Test
Mesle 'Can Opener'
Metal Stamping
Microindentation
Micro-scratch
Microtribometer
Microwedge scratch
Modified Ollard
Modified Pull Test
Moment

Nailhead
Nailhead Lead Tension Test
Nano-indentation
Napkin Ring
New Jersey Zinc Co. Test
New York Club Chisel
New York Club Tensile Method
NMP (*N*-methyl pyrrolidone)
Nodule
Normalized Sticking Tape
Notch
Nucleation

OEMS
Ollard Method
Ollard (Modified) Method
Olson Ball + Tape
Orange Peel Meter
Outboard Wire Peel

Parallel Gap Welding
Parallel Scratch
Parking Lot
Particle (Solid) Erosion
Pascoe Torque
Pass Test
Peel
Peel with Spatula
Pen Knife
Pencil
Pencil Hardness
Pendulum
Pendulum Scratching
Photoacoustic Pulse

Table 1.

(Continued)

Photothermal Radiometry
Pin-Pull
Ploughing
Plug Pull
Pneumatic Adhesion Tester
Pocket Knife
Pocket Scrape
Portable Pull Tester
Pre-cut Scrape
Pressure Cooker
Pressure Sensitive Tape
Princeton Adhesion and Scratch Tester
Pulling-down
Pull-off (Schmidt, Hoffman)
Pulsed Electron Beam
Pulsed Laser Beam
Push-in
Push-out

Q-Meter
Q-Tip
Quad Sebastian Tester

Raman Frequency Shift
Raman-Scratch
Razor Blade
Resonator Damping
Resonance Measurement (based on)
Reverse Impact
Reverse Impact + Tape
Revetest (LSRH)
RFL (British Motor Driven)
Ribbon Lead Shear Test
Ribbon Peel Test
Ring-Shear
Rivet
Rod and Ring
Rolling With Slip
Rondeau Scratch Tester
Rossman Chisel
Rub
Russian Method

Salt Bath
Sand Erosion
Sandwich Pull-off
Saw
Scalpel
Scanning Acoustic Microscope

Table 1.
(Continued)

Sclerometric
Score + Salt Spray
Scotch [®] Tape
Scrape + Solvent Wash
Scraping
Scratch
Scratchmaster
Scribe
Scribe-Grid
Sebastian Tester
Self-delamination Method
Separation Method
Shear
Shear Stress Deformation
Shockwave
Simple Cut + Tape
Single Cantilever Adhesion Test
Single Edge Notched Test
Single Pass Pendulum Scratching
Soldered-Wire Tension-Peel
Solvent
Spall
Spiral Gut
Springscale Pull-off Test
Squashing
Squeezing in Compression
Stiffness
Stoneley Waves (use of)
Strain, Constant (<i>in-situ</i> SEM)
Stretch Deformation
Stretching
Stud Pull Test
Stylometer
Stylus
Surface Acoustic Wave Sensor
Surface and Interfacial Cutting Method
Swab
Sward Adhesion Tester
Taber Scratch-Shear
Tape
T-Bend + Tape
TC Peel
Tear Test
Tensile
Tensile Extension
Tensile Shear
Thermal
Thermal Cycling

Table 1.
(Continued)

Thermal Gradient Adhesion Meter
Thermocompression Bended Peel
Thermoreflectance
Three-Point Bending
Three-Point Flexure
Threshold Adhesion Failure
Thumbnail
Tipple
Tooke Inspection Gage
Topple
Torque Wrench
Torsion Balance
Torsion Elcometer Adhesion Tester
Transient Joule Heating
Twisting
Twisting Cork
Twisting-off
Ultracentrifugal
Ultrasonic Pulse-Echo
Ultrasonic Resonance
Ultrasonic Surface Wave
Ultrasonic Vibration
Ultrasound (use of)
Undercutting
Uniaxial Compression
Uniaxial Tension
Van Laar Scratch Test
Vibratory
Voltage-Cyclic Technique
VTT Scratch Test
V(z) Curve Method
Water (boiling)
Wedge Bend
Wedge Bend + Tape
Wedge Insertion
Weight-fall
Westinghouse Scratch Meter
Weyerhaeuser Paint Adhesion Tester
Whirling Ball
Window Adhesion Test
Wire Bend
Wire Peel
Wolf Adhesion Chisel Test
Wrapping
X-Cut Tape Test (ASTM D3359-78)
X-ray Diffraction

5. CONCLUSIONS

1. There exists a plethora of techniques for practical adhesion measurement of films and coatings; however, there is no single technique which will be acceptable to everyone or will be applicable to all coating-substrate combinations. Apropos, it would be highly desirable to have a nondestructive and quantitative way to assess fundamental or intrinsic adhesion, which signifies the energy required to break bonds exclusively at the weakest plane in an adhering system.
2. For relative purposes, any of these techniques can be used. In other words, any of these techniques will rank coating-substrate samples in a series, or discriminate cases of poor practical adhesion.
3. While reporting practical adhesion values, all the parameters which can influence the results obtained using a particular technique must be specified.
4. Along with practical adhesion values, one should also comment on the locus of failure and how it was determined.
5. The best test for practical adhesion measurement is the one that simulates usage stress conditions as closely as possible.

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Adherence* failure and measurement: some troubling questions

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Abstract—It is pointed out that many methods used to determine the adherence of films and coatings to their substrates are inadequate. Sometimes, they are misleading. Key test conditions must appropriately simulate the conditions of service under which adherence failure may be brought about. It is indicated that the test environment and the rate and mode of stress application are among the important factors to consider. The nature of adherence failure is discussed against a background of multibarrier fracture kinetics. A brief review of multibarrier fracture kinetics as it applies to adherence failure and testing is given. Some evidence is cited to show that competitive failure mechanisms operate in many cases of adherence failure, and that which mechanism dominates depends on the conditions of failure.

Keywords: Adherence; adhesion; fracture kinetics; subcritical failure processes; coatings.

1. INTRODUCTION

It has already been pointed out by earlier writers that the terms *adherence* and *adhesion*, as used apropos of coating–substrate systems, have many semantic difficulties (e.g. [1, 2]). For instance, *adherence* was recognized as a term with broad meaning by Andrews [1] in his treatment of porcelain enamel coatings on a metallic substrate. He reported that in his time enamellers considered adherence to mean the ‘... resistance of the enamel to mechanical damage by impact, torsion, bending or heat shock.’ At times, adherence was taken to mean ‘... the actual attraction of the enamel and the metal to each other.’ Andrews also stated that ‘... the most common acceptance of the term is that adherence involves the resistance of the enamel coating to mechanical damage and whether the enamel comes off the metal leaving it clean or leaving variable degrees of broken glass retained in contact with the metal.’ Meanings cited by Andrews for coating–substrate adherence were not limited to enamel–metal systems. Rather, they have been used in connection with various types of coating–substrate combinations; e.g. ceramic and/or metallic coatings applied to a metallic substrate by thermal spray methods [3], and ceramic coatings put down by chemical vapor deposition [4]. In the case cited last, the authors used the terms adherence and adhesion interchangeably.

Mittal [2] dealt with the term *adhesion* by dividing it into three categories: namely, (1) *basic or fundamental adhesion*, (2) *thermodynamic or reversible adhesion*, and

*The rationale for use of the word ‘adherence’ is given in the text.

(3) *experimental or practical adhesion*. *Basic or fundamental adhesion* was ‘... related to the nature and strength of the binding forces between two materials in contact with each other.’ Mittal cited as types of bonding included in his definition of basic adhesion the following: ionic, covalent, coordinate, metallic, hydrogen and van der Waals forces. It was pointed out that ‘... this basic definition of adhesion is not very helpful as it is not possible either to calculate the magnitude or to measure such adhesion forces in practical systems.’

Thermodynamic or reversible adhesion was defined in terms of the reversible work of adhesion, W_{AB} , defined by equation (1),

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}, \quad (1)$$

in which γ_A and γ_B represent, respectively, the specific surface free energies of substances A and B, and γ_{AB} represents the interfacial specific free energy. In some cases, this definition is not useful. If at least one of the phases involved is a liquid, however, equation (1) may be useful. That is, surface tensions of liquids and contact angles generally are easily measured. Thus, if θ is the contact angle and γ_B is taken to be the specific surface free energy of the liquid phase, then

$$W_{AB} = \gamma_B(1 + \cos \theta). \quad (2)$$

Mittal identified *experimental or practical adhesion* with terms such as bond strength or adhesion strength for those cases in which measurement is made by some method in which the maximum force per unit area required to separate a coating from its substrate is determined. When measurement is made by a method which yields results in terms of the work per unit area required to cause coating–substrate separation, terms such as work of adhesion or energy of adhesion are used. Mittal was careful to point out that ‘... experimental values of adhesion may not have direct relevance to the basic or fundamental adhesion ...’. This is because processes unrelated to the simple separation of the coating from its substrate ordinarily act within the system during testing to confound the result. An important consequence of this is the fact that different methods for measuring adhesion often yield significantly different values for coating–substrate systems that are essentially the same. This problem is a matter of central importance in the present paper.

Some final comments as regards the terms adherence and adhesion are now appropriate: Most dictionaries treat the terms as being synonymous in the technical context (e.g. [5–7]). However, I use adherence more broadly than the term adhesion. *Adherence includes but is not limited to adhesion*. *Adhesion failure* is taken to mean failure that is restricted to the coating–substrate interface. *Adherence failure* also includes failure that may be partially cohesive in character. It is not infrequently observed that some portions of a crack front in a coating–substrate system move through the interface while other portions are moving through the coating and/or the substrate. In some instances, there may be multiple cracks moving within the same time frame to make up the major crack front, some at the interface and some within the near-interface bulk phases. In this paper, such complicated failure is called adherence failure. Adhesion failure is taken to be that which occurs strictly at the coating–substrate interface or within the interfacial region.

In the late 1950s, adherence testing of ceramic or vitreous coatings on metallic substrata was typically done by methods that left much to be desired. In one test, for example, a known weight (often a ball bearing) was dropped at a right angle from some predetermined height onto the exposed surface of a coating that was to be checked (e.g. [8]). If no fracture occurred in the coating, owing to the impact of the weight, its adherence to its substrate was deemed satisfactory. On the other hand, if fracture was observed, the area of coating dislodged from the substrate in the locality of the point of impact was taken as a crude measure of the lack of adherence of the coating to its substrate. One engineer that I met used a silver dollar for the weight in his test. In a somewhat similar approach, a ball bearing was pushed against the coating surface under a predetermined static load (e.g. [9]). Again, if no fracture occurred, the coating–substrate adherence was considered adequate. Fracture of the coating was interpreted as an indication of unsatisfactory adherence. Such tests often yield confusing results that provide little insight. Nevertheless, some who used them were convinced of their validity. It was about this time that various pull-off tests were first advanced. Many other kinds of tests to measure adherence then came along; moreover, the understanding of adherence increased. Even so, problems regarding adherence and its measurement remain unresolved as the present paper is written.

Quantitative determination of the adhesion between coatings (or films) and their substrates is a matter of considerable practical importance. If coatings or films fail to adhere adequately to their substrates during service, functions for which they are applied may not be achieved. It is often necessary that adherence testing be included in quality control procedures. Furthermore, scientific investigation into the nature of coating–substrate adherence and the development of strategies to improve it require its accurate and meaningful measurement. More than 200 different test methods have been advanced for one or more of these purposes [1, 2, 10–16]. Some of these are inadequate on fundamental grounds. In addition to being fraught with the kinds of complications that distinguish practical adhesion from basic or fundamental adhesion (see above), some methods may not provide any valid measurement of the adherence. Or the conditions under which some tests are made may hopelessly confound the results. Other methods appear to be valid, but only within very limited contexts. Troubling questions and problems remain unresolved. Some of these are as follows:

- (1) Testing often is limited to ordinary temperatures. Service may occur at elevated temperatures. How does temperature affect adherence? Do adherence tests made at ordinary temperatures adequately represent adherence failure conditions at elevated temperatures?
- (2) Service conditions often include environmental factors of a chemical nature (e.g. moisture or sulfur oxides) that may affect adherence. Nevertheless, adherence testing conditions may not take adequate cognizance of such factors.
- (3) The adhesion of a coating to its substrate may increase [17] or decay [18–21] with time, following coating application, depending on the nature of the system and the conditions imposed during storage and/or service. Moreover, the stress level to which a given coating–substrate system is exposed during coating application, storage, and/or service may affect the direction of such change and the rate at which it occurs (e.g. [19–21]).
- (4) A key question is this: ‘Is coating–substrate failure ever truly interfacial in character?’ This matter needs to be considered carefully [1, 2, 13, 22–24]. Stress level

and loading rate have been observed to affect the path taken by the major crack during the failure process and, hence, the measured adherence [19–21, 25]. Much testing of adherence fails to take these facts into account.

- (5) Some methods used for testing adherence apply stress or energy unevenly to the coating–substrate interface in an unacceptable measure. One important consequence of this in some cases is that the stress or energy density at the locus of failure initiation is not really known. Hence, the value calculated for the adherence from the data obtained, using the conventional formulas for the case, may have an unacceptable, and often unrecognized, error associated with it.
- (6) Methods used for testing adherence (e.g. [1, 2, 10–13, 15, 16]) yield results that seem to differ importantly as regards their fundamental meanings. For instance, tensile pull-off test results have dimensions of M/Lt^2 whereas data obtained by the impact deceleration test or the widely used peel test have dimensions of M/t^2 . The scratch test yields data with dimensions of force, ML/t^2 . L , M , and t represent the dimensions length, mass, and time, respectively. Other tests may give data with still different fundamental dimensions. Another problem: The literature dealing with measurement of adhesion and/or adherence reveals confusion in this regard on the part of too many workers; i.e. dimensions cited with data too often are incorrect.
- (7) Are the samples tested truly representative of the coating–substrate system that will see service? This matter is complicated by the fact that adherence failure — even that which occurs altogether at the coating–substrate interface — follows extreme value statistics [19, 26]. Can proof testing be used?
- (8) If the coating–substrate interface is not smooth but irregular, stresses at the crack front during adhesion failure may be more complex than assumed. This could lead to misinterpretation.
- (9) Undetected residual stresses within the coating–substrate system may affect adherence and confound adherence testing.

It is the intent of this paper to discuss the questions and problems in a fashion that will stimulate further in-depth study of adherence testing and the interpretation of its results. Detailed treatment of some issues is beyond its scope; earlier authors have discussed them (e.g. [2, 11, 24]). Moreover, an extensive bibliography [13] and critical reviews (e.g. [2, 10–12, 15, 16, 27]) of most methods used for adhesion and/or adherence testing have already been published and will not be dealt with extensively here. Testing methods will be described only to the extent necessary to facilitate presentation of the ideas broached here.

2. DISCUSSION

2.1. *Testing at ordinary temperatures vs. service at elevated temperatures*

That temperature can affect coating–substrate adherence seems quite obvious. The mechanical properties of most materials change with temperature, albeit not always for the same reasons. If a coating is intended to serve as a thermal barrier on, say, an interior surface of a jet engine or rocket thrust chamber, its mechanical properties including the coating–substrate adherence are likely to vary widely from those measured at ordinary temperatures. Moreover, stresses that derive from temperature gradients and differences

in thermal expansion properties will develop in service that are not taken into account in typical adherence tests. These stresses will affect the coating–substrate adherence. In some instances, more or less ductile bond coats can be used to dissipate to some extent the stresses developed. Even so, the pertinent question remains: ‘How should coating–substrate systems be tested for adherence if their service is to be at elevated temperatures?’

Another relevant factor that comes into play as a consequence of testing temperatures being markedly different from service temperatures stems from the fact that adherence failure often involves thermally activated rate processes. Thus, reactions that contribute to adherence failure may proceed at significantly different rates at service temperatures if those temperatures differ in substantial measure from those associated with the test conditions. This underscores the need, in some cases at least, of testing coating–substrate adherence at temperatures characteristic of the projected service.

Many tests used to measure coating–substrate adherence require the use of an adhesive (typically an epoxy or a cyanoacrylate) to attach a load-transmitting fixture to the free surface of the coating or film. This is done so that a measured tensile or shear stress can be applied to the coating–substrate system. The applied stress on the coating at the time of failure is then taken as the measure of the adherence. Examples of such tests include most of the direct pull-off methods (e.g. [28, 29]), the moment or topple method [30–32], lap shear tests [33–35], the napkin ring test [36], and certain fracture mechanics tests adapted to the testing of adherence; e.g. the double cantilever beam configuration [15, 37–47], the double torsion test [15, 38, 39, 41, 48–50], and the four-point composite bend test [19, 51]. Figures 1 through 7 respectively provide schematic representations of (1) a direct pull-off method, (2) the moment or topple method, (3) a lap shear test, (4) the napkin ring test, (5) the double cantilever beam configuration, (6) the double torsion test, and (7) the four-point composite bend test. Use of an organic adhesive for attachment of the fixture required for load transmission to the coating–substrate system limits such tests to ordinary or only moderately elevated temperatures. Yet, service conditions may often involve temperatures that are much higher, well beyond the capability of the adhesive used. In some instances, metallic brazes have been used, rather than organic adhesives, to connect the aforementioned fixture to the coating–substrate system in an attempt to extend the range of testing to higher temperatures (e.g. [52]). Even so, the test temperatures possible in such cases are often well below those met with in service.

There are other difficulties that emerge as regards the use of organic adhesives or brazes as just described. For instance, the characteristics of the adhesive affect significantly the measured value of the coating–substrate adherence for at least some ceramic–metal systems [19]. This effect is observed even though (1) there is no penetration through the coating by the adhesive and (2) failure does not occur at all near the glue line. Thermal expansion/contraction coefficients of brazes are such, compared with ceramics, that when they are used to attach a load transmission fixture to the coating surface in ceramic–metal, coating–substrate systems, they tend to set up residual stresses that seriously affect the measured values of adherence. Most of the reported adherence data that were obtained using an organic adhesive or braze for attachment failed to take these matters into account.

It is true that the maximum stresses which tend to cause coating failure by spallation may occur at comparatively modest temperatures during the heat-up portion of the

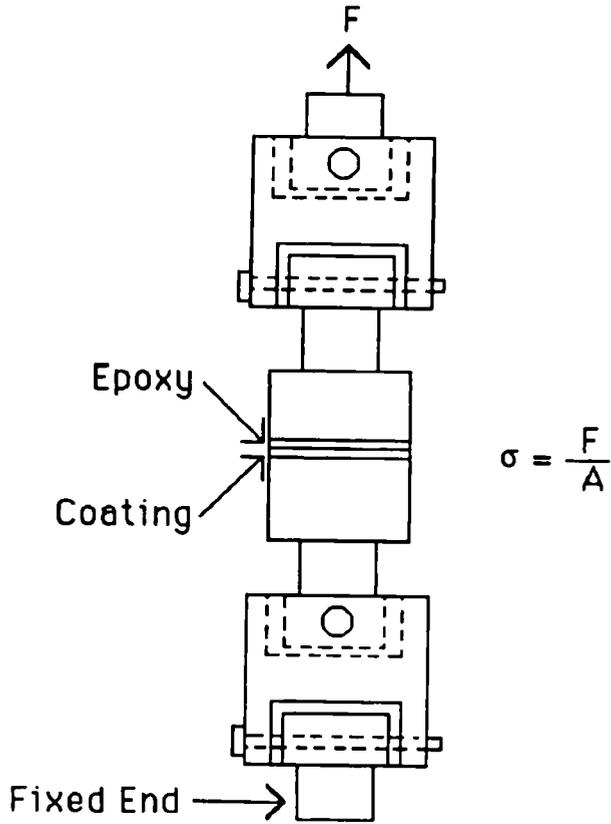


Figure 1. Direct tensile pull-off test (ASTM C633-79). This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

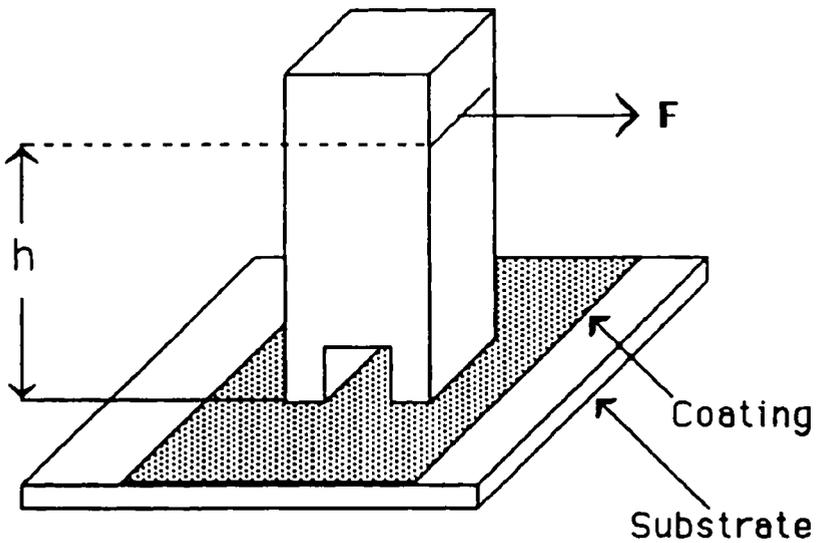


Figure 2. Moment or tople adhesion test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

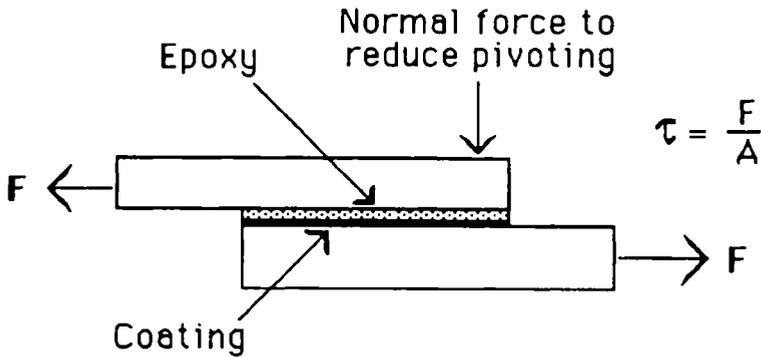


Figure 3. Lap shear test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

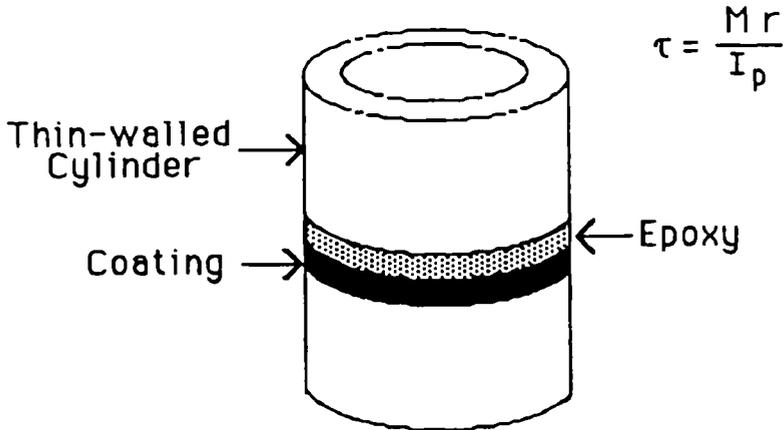


Figure 4. Napkin ring test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

service cycle. It is also true that the maximum stresses tending to cause tensile cracking of the coating may occur, again at comparatively modest temperatures, during the cooling portion of the cycle. This is particularly the case if the system is quenched. Nevertheless, it is also a fact that in many instances, significant stresses may occur at coating–substrate interfaces owing to temperature gradients that exist at the maximum service temperature. For instance, heat may be removed from the back surface of a substrate by a coolant, and this would result in a temperature gradient across the coating–substrate system. In the absence of any mechanism provided to avoid and/or reduce thermal stresses (e.g. grading the coating with substrate metal to minimize thermal expansion mismatch, or use of a highly ductile bond layer between the coating and substrate), this temperature gradient may lead to failure. Mechanical strains may be generated in substrates during service at high temperatures by factors such as impact, pressure and pressure fluctuations, and vibration. As pointed out before, material properties such as elastic modulus, strength, and toughness can change, sometimes dramatically, as the temperature is increased. It is likely, therefore, that adherence will change as well. The key question here is this: ‘How can adherence be determined

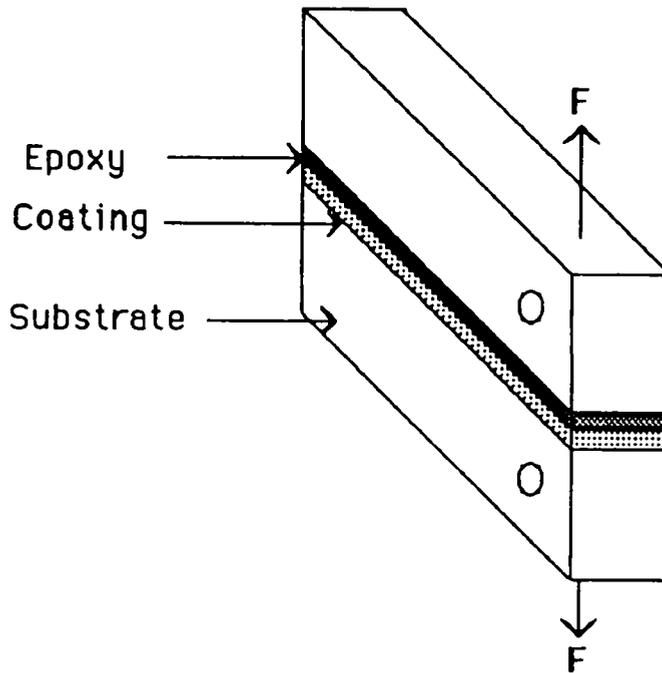


Figure 5. Double cantilever beam (DCB) configuration. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

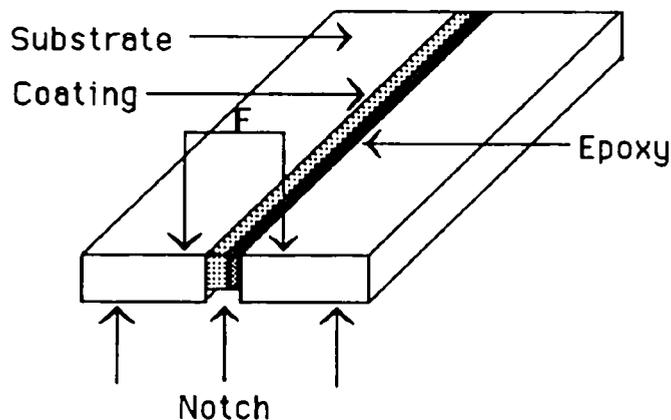


Figure 6. Double torsion test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

reliably at the high temperatures typical of those encountered under some conditions of service?'

2.2. Possible methods for testing at elevated temperatures

There are adherence testing methods that do not rely upon adhesives or brazes for attachment. Examples are the modified Ollard test [10–12, 15, 16, 53], the rod and

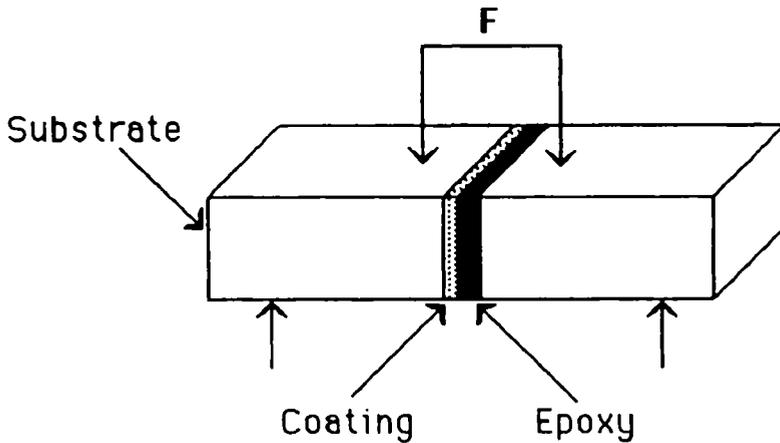


Figure 7. Four-point composite bend test (FPCB). This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

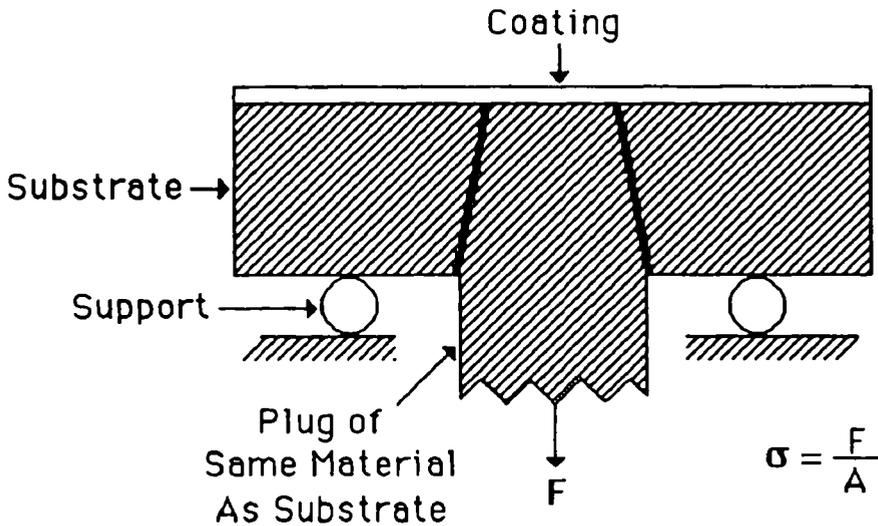


Figure 8. Modified Ollard test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

ring test [15, 16, 54, 55], the impact deceleration method [15, 16, 25, 56–59], the scratch test (e.g. [11, 15–17, 60–65]), and various strain methods that rely on the response of the coating to bending, stretching, or twisting of the substrate to provide an indication of the coating–substrate adherence [10, 66–68]. Figures 8 through 11 respectively provide schematic representations of (1) the modified Ollard test, (2) the rod and ring test, (3) an impact deceleration test, and (4) the scratch test. In many respects, such methods are marked improvements over those that must use an organic adhesive or a metallic braze if the coating or film must serve at high temperatures. Even so, there are troubling problems, as described below.

Adherence failure that involves crack growth apparently conforms to extreme value statistics [19, 26]. An important consequence of this fact is that the specimen size must

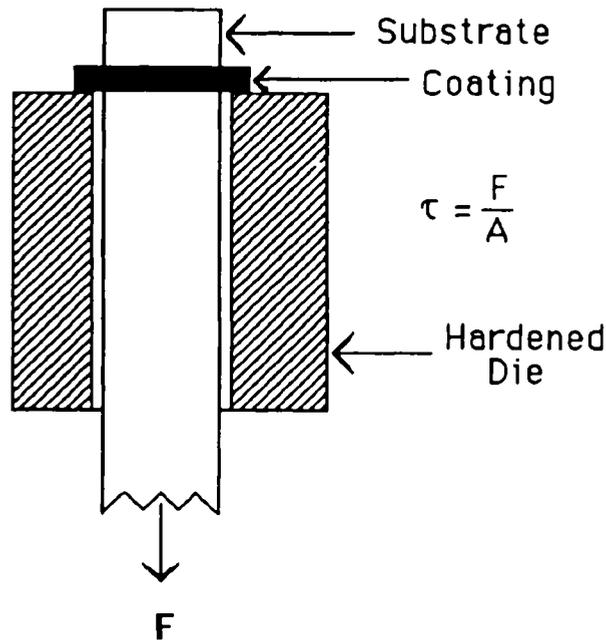


Figure 9. Rod and ring test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

be sufficiently large that a representative flaw size distribution is obtained. For example, if the tested area in a pull-off test is too small, scatter in the data becomes an important problem [28]. In the modified Ollard test, the coating tends to fail at the edges of the plug if the ratio of the interface test area diameter to the coating thickness becomes too large. In some cases, the required representative flaw size distribution simply cannot be obtained in the modified Ollard test. Another consequence of the fact that adherence failure conforms to extreme value statistics is that substantial numbers of specimens may need to be tested to achieve meaningful data. Typically, 25–50 specimens are used (e.g. [69]); however, some investigators have used 100 or more (e.g. [19]). Most users may be reluctant to conduct the number of tests required except, perhaps, to establish a sound basis for proof testing.

In some methods, a uniform lateral distribution of the applied stress over the portion of the coating–substrate interface tested is most difficult to achieve. For example, avoidance of bending moments that confound results can be a major problem in the rod and ring test. The clearance between the rod and die also must be kept to a close tolerance, otherwise thin coatings may slip through the die and/or application of force to the coating could be uneven.

The impact deceleration test has considerable potential. Nevertheless, it is not a simple test. It is not sufficient to measure only the translational velocity and mass of the coating just separated from its substrate by impact with the target [25]. The rotational velocity must also be determined. Moreover, adherence failure is abrupt in this instance and may not involve crack growth of the same kind as that associated with less rapid methods. Is the test, then, an adequate simulation of the service conditions? This question also relates to tests such as the laser spallation method [70].

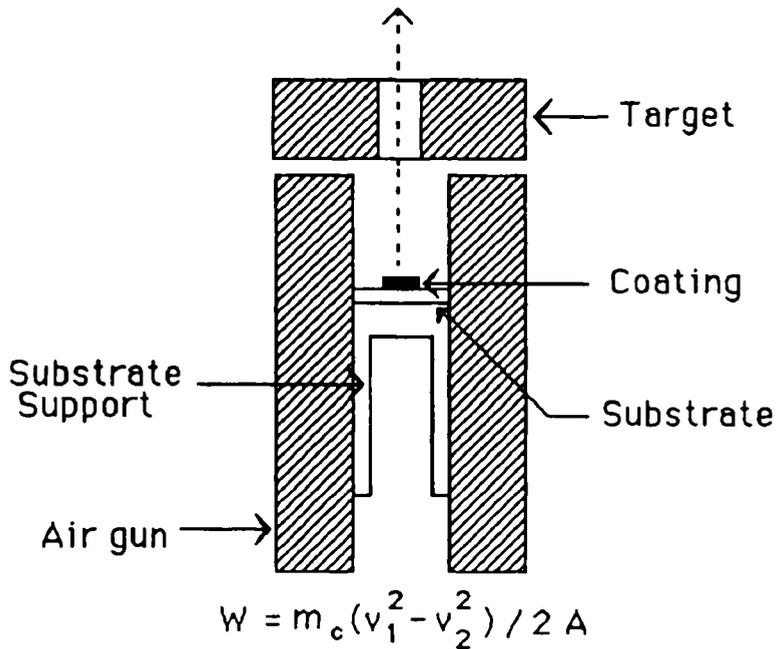


Figure 10. Impact deceleration test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

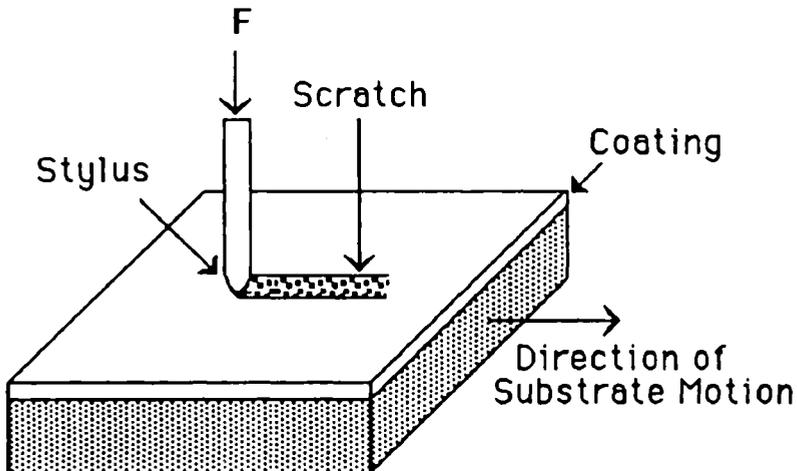


Figure 11. Scratch test. This illustration appeared previously [15] and is reprinted here by permission of the American Society of Mechanical Engineers.

The widely used and accepted scratch test does not depend on any adhesive or braze. In some of its more advanced forms, it is highly sophisticated (e.g. [62–65]). Nevertheless, the method as commonly used has many serious problems. It is altogether unsuitable for measuring the adhesion in some types of coating–substrate systems (e.g. porcelain enamels and bulk coatings such as those produced by thermal spray tech-

niques). Of course, if it is desired to measure only coating cohesion, the scratch test may be useful. However, even for cases in which many deem the test acceptable for the measurement of adhesion, an excessive fraction of the force applied to move the stylus in scratching the coating is often dissipated within the coating by cracking (if the coatings is brittle) or by plastic deformation (if the coating is ductile). This can seriously confound the results. Some of its critics (e.g. [15, 23, 61]) have concluded on rational grounds that it is an invalid method for measuring adhesion. There are, of course, some instances in which the method may be useful for qualitative, comparative purposes. Furthermore, a recent variation on the method may hold some promise [62–65]. It consists of a frictional force measurement made by a stylus that vibrates. The amplitude changes when the coating peels from the substrate. The extent to which the method can be used to measure adhesion at elevated temperatures remains to be explored. Moreover, its appropriate application may be limited to comparatively thin coatings with relatively smooth substrata.

2.3. Some miscellaneous problems

It is widely recognized that adherence may change with time if the environment to which the coating–substrate system is exposed during storage and/or service can access the interfacial region [17–21, 27, 71, 72]. In most instances, corrosion at the interface weakens adherence. For example, autoclaved, plasma-sprayed alumina coatings on 316L stainless steel or Ti-6Al-4V ELI substrates were subjected to *in vivo* aging in Sprague–Dawley rats for periods up to 29 weeks [18, 71]. Adherence, measured by the standard tensile pull-off test [28, 29], degraded markedly with time of exposure to the *in vivo* environment. Average adherence losses of 64% and 63% were observed for the specimens having substrates of 316L stainless steel and Ti-6Al-4V ELI, respectively.

Another, related problem is the fact that corrosion of elements (e.g. iron, copper) within a coating can generate stresses that impair adherence. For instance, a protective ceramic coating, graded with a metallic substrate as a means of reducing the effects of thermal expansion mismatch, may be invaded during service at an elevated temperature by corrosive species that can react with the metallic particles used to effect grading. If the volume of the solid reaction products exceeds that of the solid reactants, compressive stresses may be generated within the coating. This has resulted in coating spallation.

In other instances, even a breach in the coating or film the size of a pin prick can admit sufficient amounts of corrosive species from the environment to significantly degrade the substrate strength and/or coating–substrate adhesion within a distance of several centimeters from the breach [73]. For example, a hermetic film [polyvinyl chloride (PVC)] was applied to a glass substrate (a rod) that had been etched with hydrofluoric acid (HF) to strengthen it prior to application of the film. Subsequently, the film was deliberately punctured with a pin at a location several centimeters away from that portion of the substrate to which stress sufficient to cause fracture eventually was applied. A substantial (approximately 690 MPa) weakening of the substrate was noted within a few hours of the introduction of the breach. Presumably, moisture from the environment had passed through the breach and then diffused along the PVC–glass interface to flaws that earlier had been blunted by the HF etching. Assuming that residual tensile stresses were sufficiently proximate to some of the said flaws, the water could then react with the glass at the flaw tips to enhance their acuties and thus weaken the substrate. In the absence of the breach, no such weakening effect was observed. Admittedly, the adherence of the

PVC film to the glass was not measured in this instance. Nevertheless, it is difficult to believe that the film–substrate adherence was not similarly affected, given the propensity of water to react with glass surfaces and interfaces. Treatments used to provide hermetic seals that prevent corrosive elements from gaining access to coating–substrate interfaces may provide barriers that are vulnerable to minor mechanical damage. For instance, sealing treatments are sometimes given to anodic spark deposited films or coatings put down by a thermal spray method because it is recognized that these kinds of coatings tend to be porous. If the hermetic seal is breached, even to a minor extent, interfacial weakness may develop within comparatively short periods of time owing to the subsequent invasion of corrosive species from the environment.

The point is that the chemical characteristics of the storage and/or service environments to which a coating–substrate system is subjected can have a dramatic effect on its adherence. This is not new information. Yet, it is often found that adherence testing reported in the literature fails to take cognizance of this important fact.

One problem associated with the tensile testing of brittle materials, and this includes the tensile pull-off methods frequently used apropos of ceramic–metal coating–substrate systems, is that of improper alignment of the specimen [74]. Such adherence measurement methods as the nail-head lead tension test [75], various peel tests, and the lap shear test may also suffer from this problem. A key consequence of improper alignment is that the stress at the locus of failure is not known with sufficient accuracy. The problem becomes particularly severe when stress corrosion enters into the picture [19]. Inasmuch as many adherence tests are performed in ordinary air environments (which usually are moist), this problem is one that deserves consideration. If the coating–substrate system must serve in some corrosive environment, then that environment should be simulated appropriately in the testing effort (e.g. [19–21, 26, 49, 50, 71]). Moreover, measures need to be taken to ensure that the test and setup selected permit the stress at the locus of failure to be known with sufficient accuracy.

2.4. Crack paths during adherence failure

It is commonly observed, at least in some coating–substrate systems, that adherence failure yields a substrate-side fracture surface that exhibits patches of the coating as well as bare areas of the substrate. Under some circumstances, patches of substrate material may be found adhering to the coating–side fracture surface of a coating or film that has been removed from its substrate. Scrutiny of the fracture surface of systems that apparently have fractured cleanly at the interface of a coating–substrate system not infrequently reveals very thin films or patches from the coating remaining on the substrate. Such observations raise questions regarding the mechanism of adherence failure. Moreover, an old question is resurrected: ‘Is coating–substrate failure ever truly interfacial in character?’ This question has been actively argued (e.g. [22–24]).

Useful insight into the nature of adherence failure can be gained from investigation of subcritical crack growth in ceramic–metal coating–substrate systems. For instance, in systems consisting of plasma-sprayed alumina coatings on either 316L stainless steel or Ti-6Al-4V ELI metallic substrates, the paths taken by cracks during subcritical adherence failure were found to be dependent on the magnitude of the applied stress and/or the rate of crack propagation [19–21, 26, 49, 50]. Note that these systems were exposed to chemically active environments (namely, water and aqueous solutions) that could access the interfacial region. Figures 12 through 15 show static fatigue data obtained by

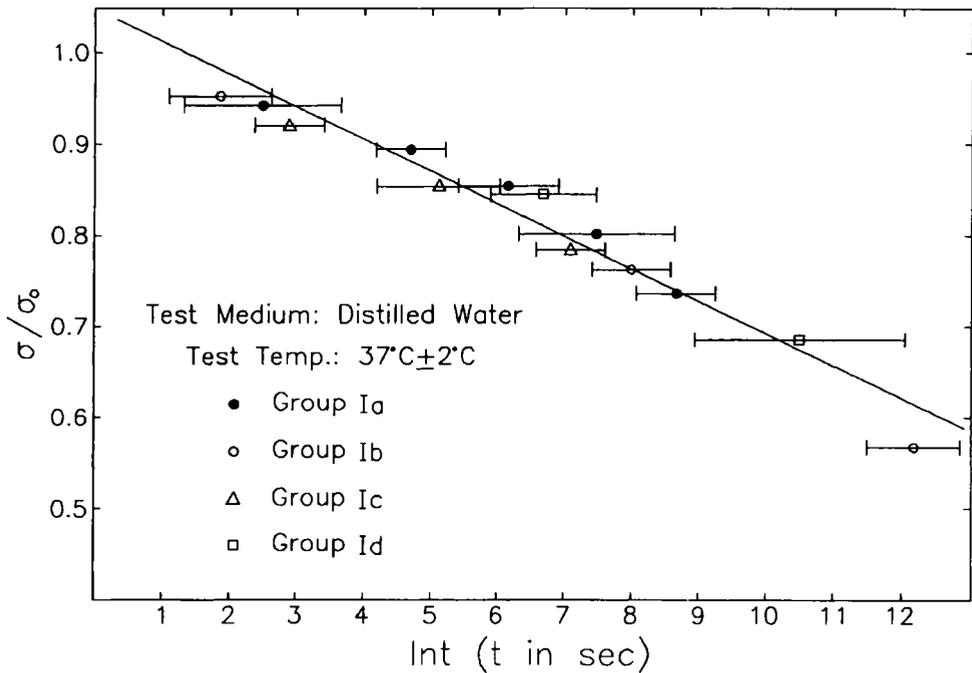


Figure 12. Static fatigue results for plasma-sprayed alumina-coated Ti-6Al-4V ELI substrates exposed to distilled water at 37 ± 2°C [19, 20]. The four-point composite bend test was used to obtain the data. This illustration appeared previously [20] and is reprinted here by permission of the American Ceramic Society.

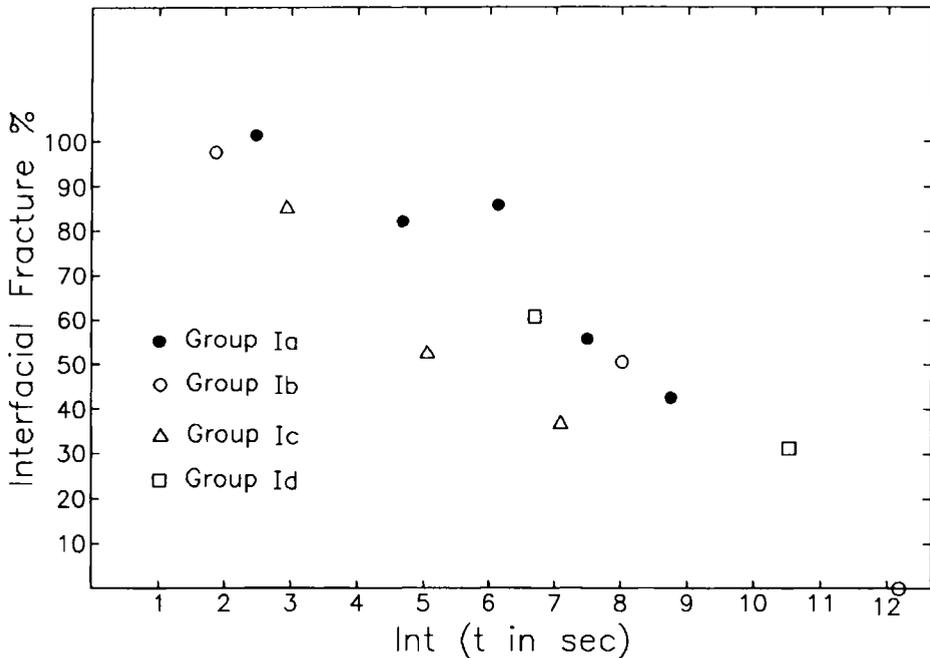


Figure 13. Time to failure dependence of the percent interfacial fracture associated with the static fatigue data of Fig. 12 [19, 20]. This illustration appeared previously [20] and is reprinted here by permission of the American Ceramic Society.

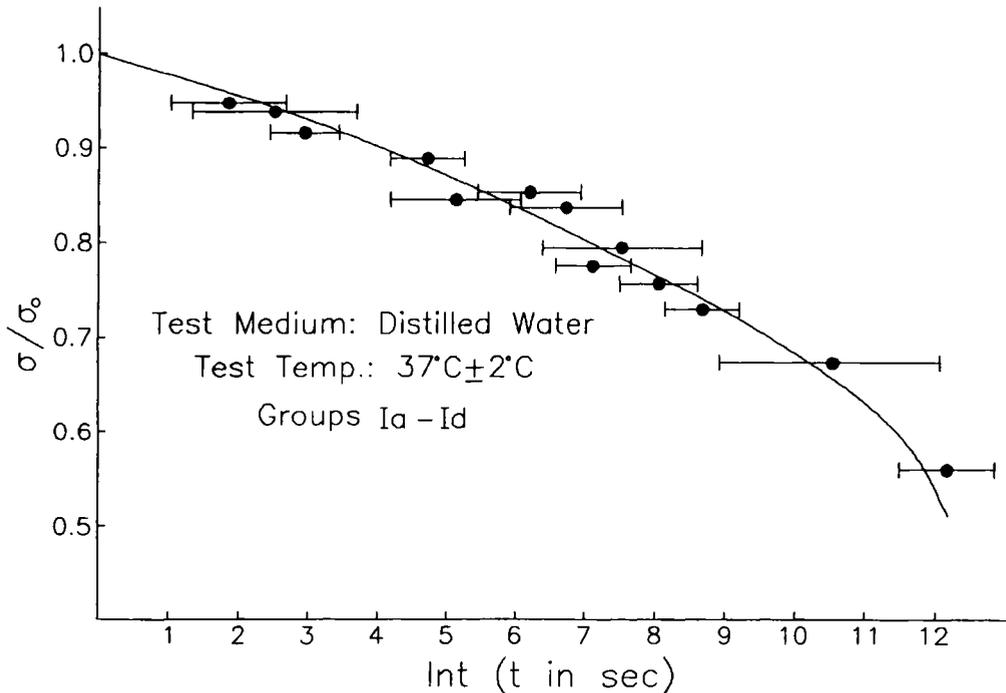


Figure 14. Optimal fit curve for the data shown in Fig. 12. The curve was obtained by cubic regression analysis [19, 21]. This illustration appeared previously [21] and is reprinted here by permission of Elsevier Sequoia S.A.

Ferber [19] for plasma-sprayed alumina coatings on Ti-6Al-4V ELI substrates. The four-point composite bend test (see above) was used for the purpose. Note that in all cases the environment was distilled water at $37 \pm 2^\circ\text{C}$, and that all four figures represent the same set of data (a total of 76 specimens). These data show trends that are similar to those revealed by other data taken at different temperatures, in a range of different aqueous test media, and/or for alumina-316L stainless steel coating-substrate systems. Rapidly propagating cracks tended to move mostly along the ceramic-metal interface; slower cracks, through the ceramic coating, roughly parallel to the coating-substrate interface (cf. Figs 12 and 13). Cracks having intermediate propagation rates left visible evidence of having propagated stochastically both along the interface and through the coating. Post-failure examinations of the fracture surfaces, interpreted within the framework of multibarrier fracture kinetics (see below), indicated that competitive fracture processes were operative at all propagation rates. Another clue to the operation of competitive fracture processes is that when the velocity of the crack that acts to separate the coating or film from its substrate is plotted against the applied stress (or the stress intensity factor), the more rapid process within a given regime is most often seen to dominate (cf. Figs 13, 14, and 15). Careful examination of Figs 12 and 14 reveals that the data points in the two figures are the same; the lines, of course, are different. The optimal fit of the data (indicated by the curved line in Fig. 14) was obtained by cubic regression. Figure 15 was derived from Fig. 14 by the method of Fuller [76]. It is interesting that the slope of the line in Fig. 15 increases for failure that occurs predominantly at the coating-substrate interface, and that it is steeper than that portion which pertains

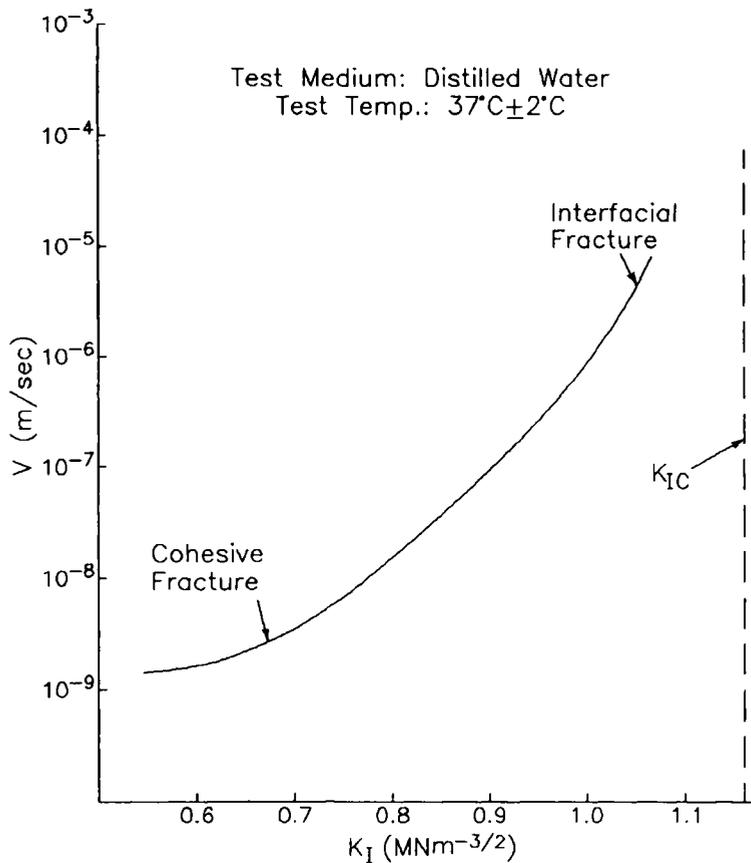


Figure 15. $V-K_I$ curve obtained from the static fatigue data of Figs 12 and 14 by Ferber [19] using the approach of Fuller [76]. This illustration appeared previously [21] and is reprinted here by permission of Elsevier Sequoia S.A.

primarily to cohesive failure. This fact will be revisited shortly apropos of the activation volume. It has interesting implications as regards the mechanism.

Of course, if the coating-substrate bonds are sufficiently weak compared with the bonds within the coating or substrate, the crack will be expected to move only along the interface. In such instances, evidence for other, competitive processes would not be seen because the process at the interface would dominate under all conditions. Nevertheless, coating-substrate separation that is absolutely clean, with no fracture occurring either within the coating or within the substrate, is rarely, if ever, achieved.

Evidence of competitive fracture processes is also observed in some polyphase solids. What is observed in such systems may provide insights that can apply to coating-substrate systems. For example, processes that participate in intergranular fracture, on the one hand, and those that lead to transgranular fracture, on the other, are often seen to be competitive. The fracture of MDF (macro-defect-free) cement is a case in point [77, 78]: Comparatively slow crack growth usually results in intergranular failure. That is, the crack tends to pass around the ceramic grains of the cement and through the polyvinyl alcohol phase. As the crack propagation rate is increased, a gradual transition from intergranular to transgranular failure occurs. At comparatively high

crack growth rates, failure is predominately transgranular. Numerous other polyphase and/or polycrystalline materials exhibit similar behavior. However, there are systems and conditions in which one mode of failure or the other predominates regardless of the strain rate (e.g. [79]). If phase changes are initiated as the crack passes through a particular region of the solid, this further complicates the picture. Nevertheless, the fact that competing processes operate in many instances is clear. It is interesting that within the aforementioned transition zone, portions of a single crack front may exhibit both intergranular and transgranular fracture, and that this pattern may change with time as the crack propagates through the material. This suggests that either or both of the following conditions may exist: namely, (1) the character and/or properties of the material encountered by the crack as it moves through the solid are not uniform, and (2) the energy available to drive the crack propagation is not uniform in time or space along the crack front. Nonuniformity in the concentrations of environmental species along the length of the crack is also expected to influence the paths taken by various segments of a crack front. Fractographic evidence for this was found in connection with crack propagation in glasses [80].

Admittedly, the MDF cement case just cited does not involve a coating–substrate system of any kind. The example nevertheless provides additional evidence that the paths taken by cracks propagating through a material of more than a single phase may depend on the crack velocity (which is a function of the applied stress), among other factors. It is quite evident from the data in Figs 12–15 that competitive adherence failure processes operated in the thermal spray coating–substrate system that was investigated. The MDF cement example is helpful because it suggests that competitive failure processes may occur in various other systems that involve two or more solid phases. In fact, data reported by Oh *et al.* [81] on subcritical stress-corrosion crack velocities along plain and chemically etched glass–copper interfaces (their Fig. 7) gave clear evidence to me that both sequential and competitive adherence failure processes were active in each case. How prevalent such effects may be in the adherence failure of ceramic–metal, coating–substrate systems other than those mentioned here is not yet known. Even so, this places additional emphasis on the importance of adequate simulation of service conditions in adherence testing. It also raises some most interesting questions of a scientific nature. For instance, is the local energy density uniform along the front of a propagating crack, as has often been assumed, even when the applied stress is constant? Can variations of material character and/or properties be determined quantitatively from microanalysis of the fracture surfaces of specimens, and then related to local variations in the fracture process? It can be shown that the slope of the $\ln V$ vs. σ (or $\ln V$ vs. K_I) curve is proportional to the *activation volume* [82]. Here v and σ represent the crack front velocity and the applied stress, respectively; and K_I is the mode I stress intensity factor. What is implied, then, by the fact that the slopes of curves that represent failure at or very near coating–substrate interfaces are often greater than those that represent cohesive failure within the corresponding coatings (e.g. [19–21])? In the context of the fracture processes that occur during adherence failure, what occurs physically when the activation volume is increased so markedly? Does it mean that patches of bonds are broken as the crack front advances near the interface whereas single bonds are broken when the crack moves through the coating at lower values of K_I ? These questions deserve investigation. Again, are the often simplistic interpretations of adherence data, which stem from the usual, so-called practical methods of testing, sufficient?

2.5. Multibarrier fracture kinetics

Many of the questions associated with adherence failure in coating–substrate systems, and the growth of cracks at and/or near solid–solid interfaces have been addressed very well in the context of fracture mechanics (e.g. [52, 83–85]). However, theory based strictly upon fracture mechanics omits aspects of the failure process that in some instances are important. This is particularly so in connection with subcritical failure. The problem is not unique to coating–substrate systems; failure of some bulk materials and fibers requires insight beyond that provided by fracture mechanics alone. Some workers have merged fracture mechanics with rate process theory in response to this need (e.g. [86–100]). In some of its later versions, the theory of multibarrier rate processes [101–103] has been melded with fracture mechanics for the purpose inasmuch as much of the data obtained indicated clearly the operation of both sequential and competitive rate processes. I have suggested the use of the term *multibarrier fracture kinetics* for the hybrid theory that has resulted [93–100] and continues in its development.

Earlier investigators of delayed failure and/or subcritical growth in glasses and ceramics recognized the need for including stress-dependent activation energies in their considerations (e.g. [86–89]). The later studies of Wiederhorn (e.g. [90–92]) provided data that in addition clearly indicated the operation of both sequential and competitive rate processes. For instance, Wiederhorn found three regions in his $\log V$ vs. K_I curves. Within region I (i.e. that just above the threshold stress intensity factor), a stress corrosion process controlled the rate at which the crack advanced. As K_I was increased, v increased until region II became dominant. Within region II, the crack velocity was controlled by the rate at which corrosive species (water in the case of Wiederhorn's data) could reach the crack tip. In cases that involved ceramics or glasses, this generally required diffusion of the corrosive species (usually water) through the gas phase in the crack and/or along the exposed surfaces at and near the crack tip. Data obtained by Williams and Nelson [104], in which gaseous hydrogen induced subcritical cracking of Ti-5Al-2.5Sn alloy, indicated that the diffusion path of the hydrogen was in the bulk metal phase vicinal to the crack tip. When the crack growth became sufficiently rapid that the rate was controlled by the diffusion of the corrosive species to the crack tip, region II became prominent. That is, the slower of the two processes — stress corrosion at the crack tip and transport of the corrosive species to the crack tip — dominated. *This is typical of sequential reactions in which the slowest step (or series of steps) controls the overall rate.*

In the case of region III, data obtained by various investigators uniformly indicated that the processes active in region III were in *competition* with those in regions I and II. That is, once K_I became sufficiently large that the transition from region II to region III behavior occurred, it was the *more rapid set of processes that dominated*. In Figs 14 and 15, it is quite clear that the data indicate a transition from the less rapid to the more rapid set of processes. In other words, the processes involved in cohesive failure are slower than those involved in interfacial failure. The two sets of processes are competitive.

Figures 16 through 18 provide additional solid evidence that the subcritical adherence failure of the plasma-sprayed alumina coating/Ti-6Al-4V ELI substrate system, discussed in connection with Figs 12–15, involved chemical rate processes. The fact that the failure process has a significant temperature dependence is shown quite amply in Fig. 16. Figure 17 shows Arrhenius plots of the same data as those illustrated in Fig. 16.

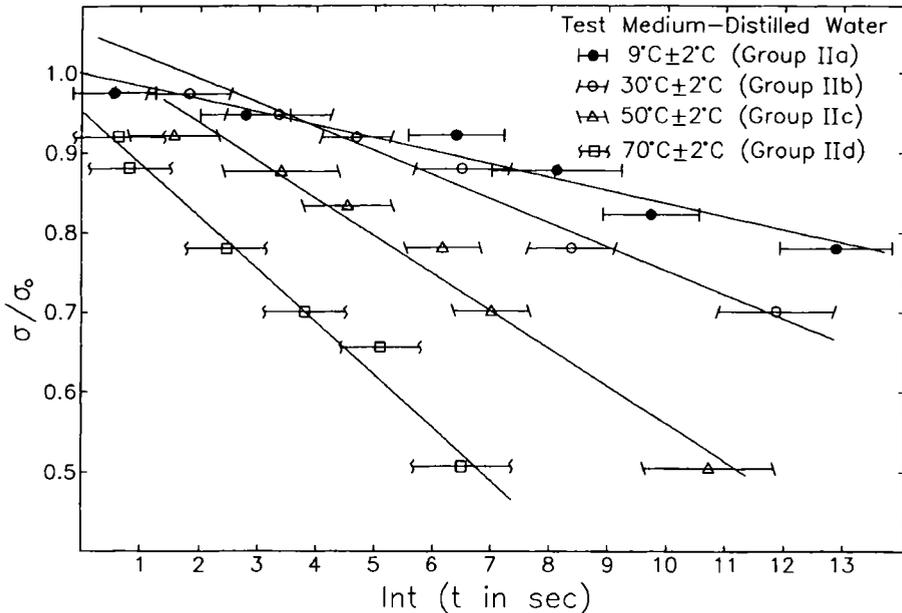


Figure 16. Temperature dependence of static fatigue failure of plasma-sprayed alumina-coated Ti-6Al-4V ELI substrates exposed to distilled water [19, 20]. This illustration appeared previously [20] and is reprinted here by permission of the American Ceramic Society.

Figure 18 is a plot of the activation energy vs. the ratio of the applied stress, σ , to that obtained for 'instant' failure, σ_0 . Note that the results for the plasma-sprayed alumina on 316L stainless steel system are included in Fig. 18 for purposes of comparison. There are at least two important facts to glean from Figs 17 and 18: namely,

- (1) The activation energies associated with the adherence failure are of such a magnitude that they can reasonably be associated with chemical reactions including the chemically assisted rupture of highly stressed bonds at the tips of cracks within the surfaces of solid phases and/or at solid–solid interfaces.
- (2) There is a significant stress dependence of the activation energy. This is compatible with the findings of certain earlier investigators (e.g. [86–92]).

The data in Fig. 18 raise some interesting questions: Why are the activation energies associated with the specimens having 316L stainless steel substrates significantly less than those with the Ti-6Al-4V ELI substrates for all values of σ/σ_0 ? Also, what causes the deviation from straight-line behavior for σ/σ_0 values less than about 0.7? These questions have not yet been answered definitively. However, it is believed that the effects of residual stresses that derive from differences in substrate properties and possibly the behavior of the epoxy adhesive used for attachment of the load transmission rod to the coating surface may be responsible. In any case, these questions do not erase the basis provided for the validity of melting fracture mechanics and the theory of rate processes.

2.6. Selection of adherence testing methods

It is widely realized that adherence test methods must be selected on the basis of the situation at hand, e.g. on the basis of the nature of the coating–substrate system to be

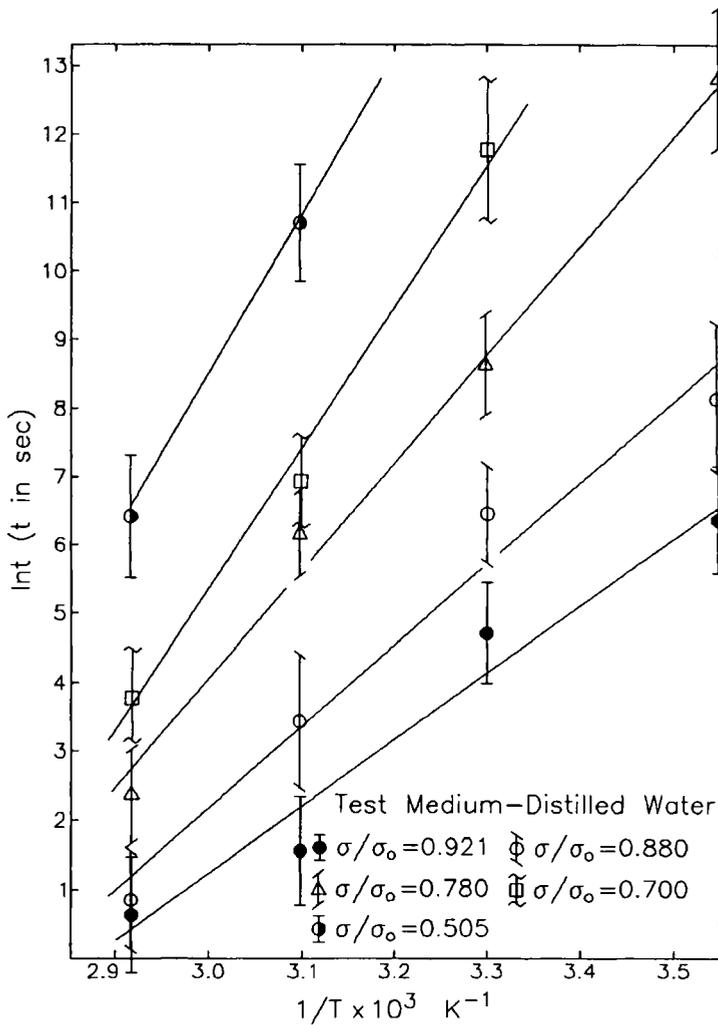


Figure 17. Arrhenius plots for the static fatigue failure of plasma-sprayed alumina-coated Ti-6Al-4V ELI substrates exposed to distilled water [19, 20]. This illustration appeared previously [20] and is reprinted here by permission of the American Ceramic Society.

tested. No universal test is available. Yet, it is troubling that the various tests that have been devised yield results that are, in many instances, basically different by nature: that is, the results achieved by some tests may differ markedly in their fundamental dimensions from those obtained by other methods. This fact alone implies certain incompatibilities amongst the methods. Moreover, attempts to reconcile the differences on any quantitative basis have seldom, if ever, succeeded. This suggests that various kinds of tests may yield different kinds of information. A tensile pull-off test, for example, will not provide the same kind of information that a scratch test will. Nor can a laser spallation method yield the same kind of information that, say, a four-point bend test does (and vice versa). The challenge, then, is to ascertain just what the test results obtained in any given case really mean. Also, there is a question that should always be addressed: namely, 'Does the test provide failure conditions sufficiently similar to

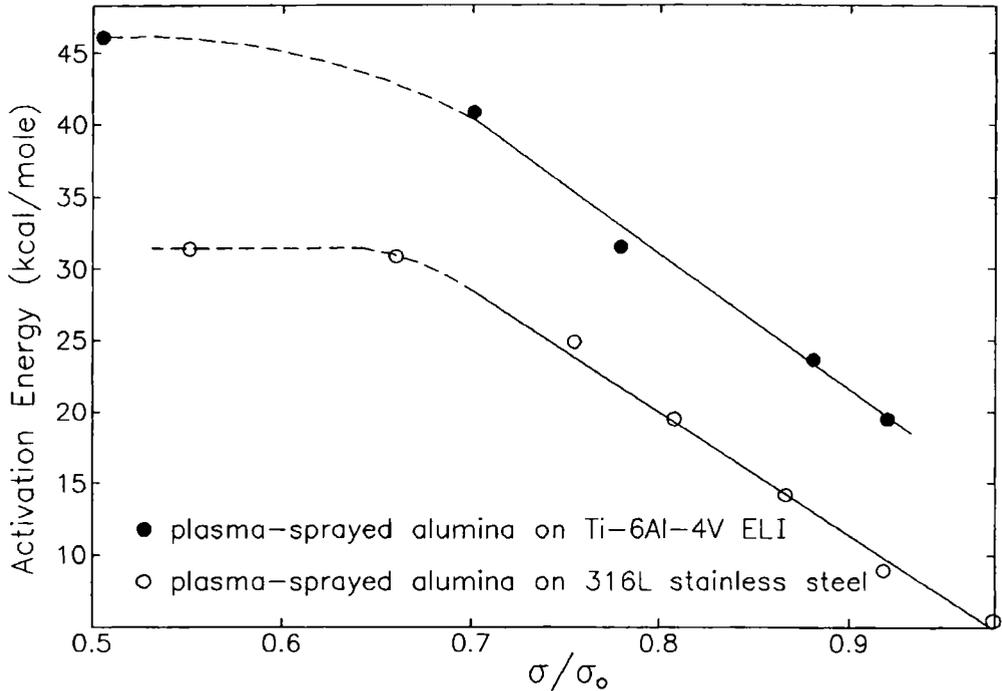


Figure 18. Stress dependencies of the activation energies for the static fatigue of plasma-sprayed alumina coatings on Ti-6Al-4V ELI and 316L stainless steel substrata [19, 20]. This illustration appeared previously [20] and is reprinted here by permission of the American Ceramic Society.

those that the system will encounter in service?' Failure processes involved in different tests may not be the same. Therefore, a major question that must be considered is this: 'What changes occur in the rate processes and fracture mechanics pertinent to adherence failure owing to differences in the nature of the tests?' The situation also poses basic questions regarding the very meaning of adherence.

Residual stresses are seldom distributed evenly over a coating-substrate interface [105, 106], nor are applied stresses [74, 105]. Even when coating-substrate systems have been annealed in some fashion, localized residual stresses may vary. Therefore, as a crack propagates through the interfacial region of a coating-substrate system, some segments of the crack front can be expected to be moving more slowly than others at any given moment; moreover, some portions will move along the interface while others will spread through either the coating or the substrate near the interface. The paths assumed by various segments of the crack front may change with time as the crack propagates. Those available paths of least resistance and/or those offering the greatest motivation will be taken by the crack. Regions within the coating-substrate interfacial space that have pores and cracks, or weakly bonded grains, will offer less resistance to the movement of the crack. Moreover, those regions with which comparatively large residual tensile stresses are associated will be more susceptible to the entry of some segment of the crack front than those having compressive or significantly smaller tensile stresses. Another complication is the fact that substrate roughness affects significantly the character and distribution of stresses at the coating-substrate interface. Finally, some segments of the crack front may be more accessible to crack-promoting environmental

agents (e.g. moisture) than others. All of these factors and others must be considered when a fracture kinetics approach is taken to explain the observed phenomena. This is anything but a simple task. Nevertheless, improved and much needed insights into the nature of adherence and its measurement can be expected to result.

3. CONCLUSION

Testing of adhesion is not yet well understood notwithstanding the considerable progress that has been made since the 1950s in the pertinent art and science. Many different tests have been devised; however, there is considerable confusion. Results from some of the most widely used test methods do not have the same dimensions, and this suggests that data from various tests may have different meanings. In a practical sense, it is vital that the test conditions simulate well the expected service conditions. Otherwise, the value of the test is brought seriously into question. Service temperature, loading, and environmental chemistry are some of the factors that must be considered. Fracture kinetics is a promising theoretical framework within which to examine both adhesion and adherence failure.

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